REFERENCES

Benedict T S & Shockley W. 1953 *Phys Rev.* **89**, 1152
Benedict T. S. 1953 *Phys. Rev* **91**, 1565
Bhar J N. 1963 *Proc IEEE* **51**, 1623
Blakemore J S 1969 *Solid State Physics*, Saunders Company, Toronto
Blatt F J 1968 *Physics of Electronic Conduction in Solids*, McGraw-Hill Book Co . Inc , New York
Dube D C & Natarajan R 1973 *J. Appl Phys.* **44** 4927
Goldley J M & Brown S. C. 1955 *Phys. Rev* **98**, 1761
Montgomery C A. 1947 *Technique of Microwave Measurements*. MIT Rad Lab. Ser New York, McGraw-Hill.

Indian J. Phys. **52A**, 572–575 (1978)

E.S.R. and optical absorption studies on two copper (II) Schiff-base complexes in solutions

M N CHARY AND B A. SASTRY

Department of Physics, Osmania University, Hyderabad-500007

(*Received* 4 *October* 1977)

As a part of our general programme to study stereochemistry and metal ligand bond nature of organo-metal complexes in solutions by physical methods, we have taken up the E S.R. and optical absorption studies of two copper(II) Schiff-base complexes (Healy *et al* 1975) formed by the condensation of 3,3′-(iminobis-propylamine) and 2-hydroxy-5-methylbenzophenone (hereafter referred to as Cu(mbp)) and 5-chloro-2-hydroxybenzophenone (hereafter referred to as Cu(cbp)). Crystal structure is available only for the former complexes (Healy *et al* 1975) From the crystal structure of this complex it is found that it is a five co-ordinate monomer formed with three nitrogen atoms and two oxygen atoms arranged in a distorted square pyramidal fashion. In this communication an attempt has been made to find out whether the coordination around copper(II) ion and the crystal structure of these complexes are same by comparing the E.S R. and optical absorption data of these complexes in solutions and powders respectively The E.S.R spectra of both the complexes in solutions of benzene, dioxane, pyridine and powders are recorded with the help of a varian E-4 x-band E.S R spectrometer using E-231 resonant cavity The errors in the calculations of g and hyperfine separation (A) will be about $\pm 0{\cdot}0005$ and $+0{\cdot}5$G respectively Optical absorption spectra of these complexes in solutions are recorded with a

Unicam SP-700 spectrometer. E.S.R. spectra has been recorded for Cu(cbp) in solutions of benzene, dioxane at room temperature and pyridine at both room and liquid nitrogen temperatures. In the case of Cu(mbp) E.S.R. spectra has

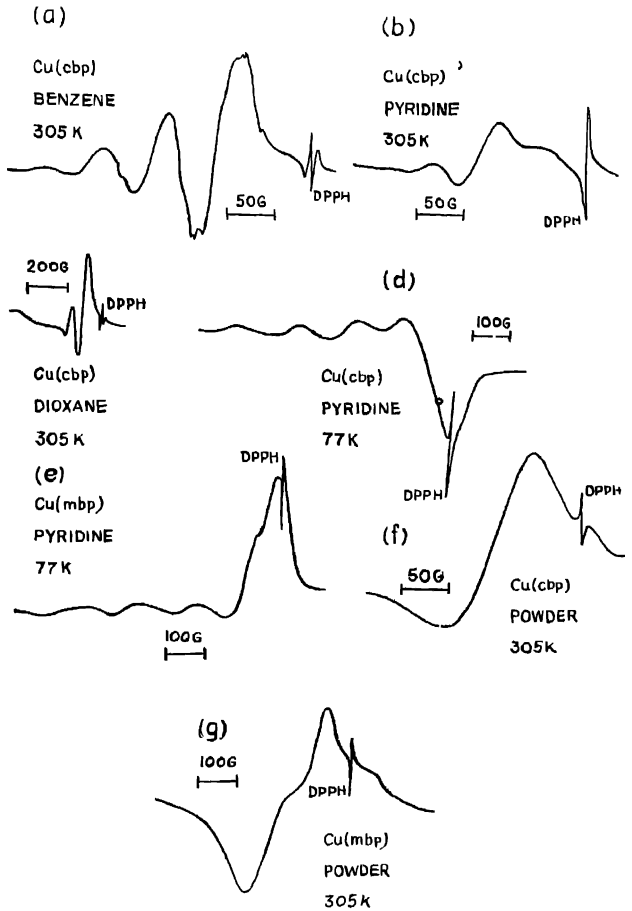

Fig. 1. E.S.R. Spectra of (i) Cu(MBP) and (ii) Cu(CBP) both at room and liquid nitrogen temperatures in different solvents.

been recorded in pyridine both at room and liquid nitrogen temperatures. The E.S.R. spectra of Cu(cbp) in benzene (Figure 1a) has given the usual four line spectra with spin-dependent line widths indicating the formation of a single

complex ion in solution. In the case of pyridine and dioxane solutions (Figures 1b and c), the spectra consists of two lines. This type of unusual solvent effects are also observed in the case of copper(II) β-diketonates (Stoklosa *et al* 1973), where bulky organic substituents are positioned on the ligand and are explained as due to the effect of viscosity, chemical exchange and anisotropic reorientation effects. The spectra of Cu(mbp) in pyridine at room temperature is not observable which may be due to large spin-lattice interaction. The frozen solution spectra of Cu(mbp) and Cu(ebp) in pyridine (Figures 1d and e) are characteristic of copper(II) ion having tetragonal symmetry. The $g_{\|}$, $g_{\perp}$ and $A_{\|}$ values of the two complexes from the above spectra are obtained using the methods of Sands and Swallen. These values along with the optical data and bond parameters are given in table 1. In the case of Cu(mbp) extra hyperfine lines from ligand

Table 1. Principal g and A values and bond parameters of Cu(mbp) and Cu(ebp) in solutions

Substance	Solvent	$<g>$	$g_{\|}$	$g_{\perp}$	$A_{\|} \times 10^4$ cm^{-1}	ΔE cm^{-1}	α^2	β^2	β_1^2
Cu(ebp)	Pyridine	2·112	2·243	2·046	−158·1 14400	12600,	0·742	0·515	0·612
Cu(mbp)	Pyridine	2·126	2·250	2·064	−156·2 14400	12600,	0·750	0·719	0·624

nitrogen atoms are also indicated on the perpendicular component of the spectrum. Such a hyperfine spectrum is also observed in the chloroform solution of this substance (Healy *et al* 1975). As is evident from table 1, the value of $<g>$, $A_{\|}$, $g_{\|}$, $g_{\perp}$ and ΔE (orbital splitting obtained from optical spectra) values for both the complexes are very nearly equal indicating that the coordination of copper(II) ion in both the complexes is almost same.

The metal-ligand bond nature of both the complexes in pyridine is calculated using M O theory put forward by Maki & McGarvey 1958 and Kivelson & Neiman 1961. Eventhough this theory is proposed to calculate the bond parameters of the planar complexes, for the sake of simplicity number of workers applied this theory for octahedral (Lewis & Alei 1966, Buluggiu *et al* 1971), and five-co-ordinate complexes (Gregson & Mitra 1968), neglecting the contribution of atoms which are out of the principal coordination plane. The relationship between principal g, E and bond parameters are given in the following expressions (Wasson & Zacharopoulos 1969).

$$\frac{(g_{\perp}-2{\cdot}00\Delta 2)E_{xz}}{1656\ \text{cm}^{-1}} = \alpha^2 \qquad \ldots (1)$$

$$\frac{(g_{\|}-2{\cdot}002)\Delta E_{xy}}{6624\ \text{cm}^{-1}} = \alpha^2\beta_1^2 \qquad \ldots (2)$$

$$\alpha^2 = -A_{\parallel}/P + (g_{\parallel} - 2) + \frac{3}{7}(g_{\perp} - 2) + 0{\cdot}04 \qquad (3)$$

where α, β_1 and β represent the σ-bond, in-plane π bond and out-of-plane π bond coefficients respectively. We have assigned that the values of optical absorption at 14400 cm^{-1} and 12600 cm^{-1} correspond to ΔE_{xz} and ΔE_{xy} respectively. Using these values, the values of α^2, β^2 and β_1^2 are calculated and are given in table 1. The values of α^2 and β_1^2 are found to be same for both the complexes. The σ-bond in both the complexes is less covalent than the in-plane π bonding. The out-of-plane π bonding (β^2) of Cu(mbp) is less covalent than that in Cu(ebp).

The E S R spectra in powders of Cu(ebp) and Cu(mbp) [Figure 1f and g] are different indicating that the crystal structure of both the complexes are different, although the coordination of copper(II) ion in both the cases appears to be same. The powder spectra represent the overall symmetry of the unit cell if it contains more than one molecule. Thus symmetry in the case of Cu(ebp) appears to be cubic (isotropic g value spectra) and in the case of Cu(mbp) is rhombic (Kneubhul 1960).

Acknowledgments

The authors are thankful to Profs Ekk Sinn and P. C. Healy, University of Virginia for supplying the complexes. We thank Prof K. V. Krishna Rao, Head of the Department, for his encouragement.

References

Buluggiu E., Dascola G., Giori D. C. & Vera A. 1971 *J. Chem. Phys* **54**, 2191
Geisman H. R. & Swalen J. D. 1962 *J. Chem. Phys* **36**, 3221.
Gregson A. K. & Mitra S. 1968 *J. Chem. Phys* **49**, 3696
Healy P. C., Mockler G. M., Greyberg D. P. & Sinn E. 1975 *J. Chem. Soc.* 691
Kivelson D. & Neiman R. 1961 *J. Chem. Phys.* **35**, 149
Kneubhul K. F. 1960 *J. Chem. Phys.* **33**, 1074
Lewis W. G. B. & Alei M. 1966 *J. Chem. Phys.* **44**, 2409.
Maki A. H. & McGarvey B. R. 1958 *J. Chem. Phys.* **29**, 35.
Sands R. H. 1955 *Phys. Rev.* **99**, 1222.
Stoklosa H. J., Huffman H. L. & Wasson J. R. 1973 *J. Inorg. Nucl Chem.*, **35**, 2485
Wasson J. R. & Zacharopoulos P. 1969 *J. Inorg Nucl Chem* **31**, 3881